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Electrochemical Investigations of Electronically Conductive Polymers. 4. By Controlling the Supramolecular Structure, Charge Transport Rates Can be Enhanced

by

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Electrochemical Investigations of Electronically Conductive
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Transport Rates Can Be Enhanced

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ABSTRACT

We have shown that electrically conductive polymers with fibrillar supermolecular structures can be prepared by synthesizing the polymer within the pores of a microporous membrane. In this paper we compare charge-transport rates in fibrillar polypyrrole with the corresponding rates in conventional polypyrrole films; charge-transport rates in the fibrillar versions were found to be significantly higher.

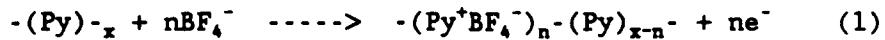
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INTRODUCTION

Electronically conductive polymers are of considerable current research interest (1). One of the most interesting features of these polymers is their ability to be electrochemically switched between electronically insulating and electronically conducting states (2). For polypyrrole, this redox switching reaction can be written as (2)



where Py and Py⁺ are reduced and oxidized monomer units in the polypyrrole film, and BF₄⁻ is a charge balancing counter-ion, initially present in a contacting solution phase.

Equation 1 shows that ions must be incorporated into, or expelled from, the polymer phase during the redox switching reaction. In many cases, the rate of this reaction is controlled by ion-transport in the polymer phase (3,4).

The switching reaction plays an integral role in nearly all of the proposed applications of electronically conductive polymers (5-7). In most cases, significant benefit would accrue if the rate of this reaction could be accelerated. The above discussion suggests that one approach for enhancing the rate of the switching reaction would be to enhance the rate of charge-transport in the polymer phase.

We have recently described a procedure for controlling the supermolecular structures of electronically conductive polymers (8). This procedure yields polymers with fibrillar supermolecular structures. In an earlier paper, we proposed that conductive polymer films with this fibrillar morphology would support higher rates of charge-transport than films with the conventional

morphology (8). To determine whether this proposition is correct, we have used an electrochemical method to compare the rates of charge-transport in conventional and fibrillar polypyrrole films. These studies have confirmed that the fibrillar films support higher rates of charge-transport. We report the results of these investigations in this paper.

EXPERIMENTAL

Reagents and Instrumentation. Pyrrole (Aldrich) was distilled under nitrogen prior to use. Tetraethylammonium tetrafluoroborate (Aldrich) was recrystallized from methanol. Acetonitrile (Burdick and Jackson, UV grade), and all other reagents were used without further purification.

All electrochemical measurements were accomplished using an EG&G PAR Model 273 potentiostat/galvanostat. The PAR 273 was driven by PAR's Headstart electrochemical software, running on an IBM PS/2 Model 50 personal computer. Gold was sputter-coated using a Technics argon plasma sputter coater. Scanning electron micrographs were obtained using a JEOL JSM-25SII microscope, in secondary electron mode, at an accelerating voltage of 25 KeV.

Nomenclature for this Paper. As indicated in the introduction, results from two different types of polypyrrole will be discussed here. These are - ordinary polypyrrole which was electrochemically synthesized at a conventional Pt disk electrode (9), and fibrillar polypyrrole which was synthesized within the pores of a host membrane (8). Throughout this paper these materials are referred to as "conventional polypyrrole" and "fibrillar polypyrrole."

Preparation of Fibrillar Polypyrrole. Fibrillar polypyrrole was prepared by electrochemically synthesizing the polymer within the pores of a microporous host membrane (8). Commercially available Anopore Al_2O_3 filters (Anotech) were used as the host membranes. These filters contain linear, cylindrical,

0.2 μm -diameter pores. The porosity is ca. 65 %; the membranes are ca. 50 μm thick. Figure 1 shows a scanning electron micrograph of the surface of an Anopore membrane.

In order to synthesize polypyrrole in the pores, one surface of the Anopore membrane must be converted into an electrode. This was accomplished using the fabrication procedure shown schematically in Figure 2. One face of the membrane was first sputter-coated with a thin (ca. 50 nm) layer of Au; this Au layer was too thin to bridge-over the pores at the Anopore surface (Figure 2b). Ag-Epoxy (Epotech 410-E) was used to attach a Cu lead wire to this Au film (Figure 2c).

The membrane/electrode was then immersed into a commercial Au plating solution (Orotemp 24, Technics, Inc.). Au was galvanostatically electroplated on top of the sputter-coated Au layer (current density = 2 mA/cm²). Electroplating was continued until the pores were completely covered with Au (5 min) (see Figure 2d). This thick electroplated Au layer was then covered with epoxy (Torr Seal, Varian). Part of the opposite (Al_2O_3) side of the membrane was also coated with epoxy so that only a 0.5 cm² area of the Anopore membrane was left exposed (Figure 2e).

An Au microelectrode is present at the base of each of the pores in the exposed portion of the Anopore membrane shown in Figure 2e. These Au electrodes were used to electrochemically synthesize a polypyrrole fiber into each of the Anopore pores. An acetonitrile solution which was 0.5 M in pyrrole and 0.2 M in Et_4NBF_4 was used for these polymerizations. A conventional one-compartment cell with a Pt counter and a saturated calomel reference electrode was employed. Polymerization was accomplished galvanostatically at a current density of 0.6 mA/cm² of exposed membrane area.

The electrosynthesis described above yields a composite of the porous Anopore host membrane and the polypyrrole fibers (Figure 2f). The host membrane was dissolved away by immersing the composite into 0.2 M NaOH for 15 min. This yielded an ensemble of isolated polypyrrole fibers, connected at their bases to the substrate Au layer (Figure 2g). An electron micrograph of such an ensemble is shown in Figure 3.

Preparation of Conventional Polypyrrole Films. Conventional polypyrrole films were synthesized onto 0.5 cm² Pt disk electrodes (9). The polymerization solution, electrochemical cell, and counter and reference electrodes were identical to those used for the preparation of the fibrillar polypyrrole. The conventional films were grown at a current density of 1 mA/cm². Film thicknesses were calculated from the quantity of charge passed during the electropolymerization (9).

After synthesis, the films were rinsed with acetonitrile, to remove unreacted monomer, and transferred to a fresh solution of vigorously degassed 0.2 M Et₄NBF₄ in acetonitrile. Oxidative synthesis of polypyrrole leaves the polymer in its oxidized (conductive) state. Prior to electrochemical characterization or analysis, the films were converted to the reduced (insulating state) by potentiostating the substrate Pt electrode at a negative potential; unless otherwise noted, a potential of -0.8 V was used.

Effect of Strong Base and Strong Acid on the Electrochemistry of Polypyrrole. Synthesis of conductive polymer fibers necessitates exposure of the polypyrrole to strong base (see above). This has a pronounced, and deleterious, effect on the polypyrrole electrochemistry (10). As part of this research effort, we had to develop a procedure to restore the polypyrrole electrochemistry. The work of Inganäs et al. suggested that the base-treated

polypyrrole might be revived by exposure to strong acid (11). We have used cyclic voltammetry to explore the effects of strong acid and base on polypyrrole electrochemistry. The intent of these studies was to develop a procedure for obtaining isolated fibers which show good polypyrrole electrochemistry.

RESULTS AND DISCUSSION

Voltammetry of Conventional Polypyrrole Films. Figure 4a shows a typical cyclic voltammogram for the reduced form of a conventional polypyrrole film. The anodic scan yields a narrow and well-defined oxidation wave. Large "capacitive-like (12)" currents are observed at potentials positive of the anodic peak; these large capacitive-like currents signal that the polymer is in the conductive state (12). The cathodic peak is typically smaller, and broader, than the anodic peak. Only (small) substrate-electrode charging currents (12) are observed at potentials negative of the cathodic peak; this signals conversion of the polymer to the reduced (electronically insulating) state (12).

It is of interest to compare this "normal" polypyrrole voltammogram with voltammograms for films exposed to strong base. To simulate the fiber synthesis procedure, an oxidized conventional polypyrrole film was exposed for 10 min. to 0.2 M NaOH. After exposure, the film was rinsed with water, rinsed with acetonitrile, immersed in 0.2 M Et_4NBF_4 in acetonitrile, and then potentiostated at -0.8 V.

When the base-exposed polymer is electrochemically cycled in acetonitrile solution, the characteristic polypyrrole redox waves are not observed (Figure 4b). Furthermore the large background currents in figure 4b suggest that the base-exposed polymer has remained in its oxidized state (13).

While the base-exposed film cannot be reduced (in acetonitrile) at -0.8 V, potentiostating at -1.4 V does cause reduction of the film (Figure 4c).

Note that the cathodic background currents in the most negative potential window (-1.4 to -1.2 V) have now been reduced to values commensurate with the reduced form of polypyrrole. Furthermore, after equilibration at this more negative potential, oxidation waves appear during the positive scans (Figure 4c). An oxidation wave initially appears at ca. -1.0 V; however, with continued scanning, this wave is supplanted by a wave at the normal (Figure 4a) oxidation potential (-0.1 V). The cathodic wave is initially poorly defined, but also shifts positively with continued scanning (Figure 4c).

We suggest the following, very tentative, model for the results summarized in Figures 4b and c. Exposure of the oxidized film to strong base causes the BF_4^- anion, initially present in the film, to be replaced by OH^- . Li and Qian also found that exposure of polypyrrole to base causes the anion initially present in the film to be replaced by OH^- (14).

Apparently, the OH^- -form of the polymer is a weaker oxidant, in acetonitrile than in aqueous solution (13); this explains why -1.4 V is required to reduce the base exposed polymer in acetonitrile (Figure 4c). Furthermore, the thermodynamics of the ion exchange reaction are such that exposure of the OH^- -form of polypyrrole to a solution of BF_4^- in acetonitrile does not cause displacement of OH^- from the film. This is evidenced by the fact that, as long as the film is not reduced, the normal polypyrrole voltammetric waves do not reappear (Figure 4b). If, however, the film is reduced (at -1.4 V), expulsion of OH^- must occur. Furthermore, reoxidation in the BF_4^- containing solution then causes BF_4^- to reenter the film; this causes the wave to shift back to its normal position. We are currently further

exploring these interesting chemical effects.

Prior studies have shown that the deleterious effects of exposure to base can be mitigated by subsequent exposure to strong acid (11). As a preliminary experiment, we investigated the effect of exposure of polypyrrole film to strong acid, without prior exposure to strong base. Figure 4d shows a voltammogram for a conventional film which had been immersed for 10 min in 1 % HBF_4 , rinsed with water, rinsed with acetonitrile, immersed in 0.2 M Et_4NBF_4 in acetonitrile, and then reduced at -0.8 V. The anodic peak is shifted slightly, and the peak current decreased, relative to the untreated film. However, the areas under the anodic waves for the acid treated and untreated films are the same. Furthermore, there is very little change in the cathodic wave.

The above study showed that exposure to acid does not dramatically alter the polypyrrole electrochemistry. A voltammogram for a base-treated film which had been subsequently treated with 1 percent HBF_4 is shown in Figure 5a. Note that the acid treatment restores the polypyrrole electrochemistry. Indeed, the voltammogram for this base then acid-treated film (Figure 5a) is essentially identical to the voltammogram for the film which was treated with only acid (Figure 4d).

Voltammetry of Fibrillar Polypyrrole Films. The investigations described above led to the following pretreatment procedure for fibrillar polypyrrole:

1. Dissolve the host membrane in 0.2 M NaOH to obtain the isolated fibers (Figure 3).
2. Immerse the base-exposed film for 5 min in 1 percent HBF_4 .
3. Rinse the acid treated film with water, then with acetonitrile.
4. Immerse the film in 0.2 M Et_4NBF_4 (in acetonitrile) and reduce at -0.8 V.

Figure 5b shows a voltammogram for a fibrillar polypyrrole film which had

been pretreated as described above. The reduction wave for the fibrillar films were consistently sharper than the reduction waves for the conventional films; in contrast, the oxidation waves are somewhat broader than the oxidation waves for the conventional films.

Evaluation of Charge-Transport Rates. Consider two polypyrrole films, one having the conventional, dense amorphous mat, morphology (15) and one in which the polymer chains are organized into discreet 0.2 μm -diameter fibers. Assume that the conventional and fibrous films contain the same total quantity of polypyrrole and that the conventional film is 2 μm thick. We suggested that the fibrillar version would support higher rates of charge transport because the dimension for ion-transport in the polymer phase changes from the full 2 μm thickness, for the conventional film, to the radius of the fiber (0.1 μm), for the fibrillar film.

In previous papers we have developed quantitative methods for evaluating the rate of charge-transport associated with the oxidation of polypyrrole (9,16). However, the rate parameter obtained applies only over a very narrow potential region at the foot of the oxidation wave. Furthermore, we do not yet have a good method for quantitatively evaluating the rate of reduction of polypyrrole.

For these reasons, we have used a large-amplitude potential step method to obtain a qualitative measure of the rate of the oxidation and reduction reactions in the various polypyrrole samples investigated here. This method entails using a large amplitude potential step to drive the oxidation or reduction reaction to completion, and following the charge-time transient associated with the redox process. Because the redox reactions are driven until the entire film is oxidized or reduced, the charge-time transients

ultimately reach a plateau value (e.g. Figure 6). The time required to achieve 95 percent of this plateau charge was used as the qualitative measure of the rate of the redox reaction.

Charge-time transients for three different types of polypyrrole films were investigated - untreated conventional polypyrrole films, base and then acid-treated conventional polypyrrole films, and base/acid-treated fibrillar films. The potential limits for the anodic steps at the untreated films were: initial E = -0.6 V, final E = +0.2 V. The potential limits for the cathodic steps at the untreated films were: initial E = 0.2 V, final E = -0.6 V.

The voltammetric waves for the treated films are shifted 50 mV negative, relative to the wave for the untreated film (see Figures 4a, 5a, and 5b). To insure that all films received the same overpotential, the potential limits for the treated films (both conventional and fibrillar) were shifted 50 mV negative of the limits for the untreated films. Note, however, that the most important comparison is between the treated conventional film and the treated fibrillar film. The same potential limits (-0.65 V to +0.15 V) were used for both, so there is no ambiguity regarding the extent of overpotential applied to these two samples.

As far as we know, results of a careful comparison of the oxidative and reductive charge-time transients for a conventional polypyrrole film have not been previously reported; this comparison (Figure 6) is quite elucidating. At short times, the reduction process is faster than the oxidation process (see Figure 6; at times less than ca. 1 sec., reductive charges are greater than oxidative charges). However, the rate of reduction ultimately slows relative to the oxidation rate (note cross-over in Figure 6). As a result of this cross-over, the reduction process always takes longer than the oxidation

process.

This interesting cross-over in the relative rates of the reductive and oxidative processes can be explained as follows. The reduction is initiated at a film which resembles a porous metal (12). This porous metal film has a high capacitance (12); thus, a large slug of capacitive charge is delivered early in the reduction process. In contrast, oxidation is initiated at an electronically and ionically insulating film. Not only is there no short time slug of capacitive charge (above that needed to charge the base electrode (12)), but the high resistance of this film insures that the initial oxidation rate is small. Indeed, the insulating film, present at the onset of oxidation, may increase (relative to the oxidized film) the uncompensated resistance. This would cause the oxidation rate to be slow, relative to the reduction rate because this uncompensated resistance is not present at the onset of reduction.

Ultimately, however, the films reverse roles. The oxidized film (present at the beginning of the reduction process) becomes reduced. This newly created electronically and ionically-insulating film slows the rate of the reduction process. Furthermore, the reduced film (present at the beginning of the oxidation experiment) ultimately becomes oxidized. This newly-created ionic and electronic conductor allows for faster, oxidative charge-transport rates to be achieved.

The data shown in figure 6 corroborate our earlier conclusion that large amplitude methods should not be used to obtain apparent diffusion coefficients D_{app} 's for electronically conductive polymers (9,16). D_{app} data are obtained from the short time chronocoulometric data. If the short time data in figure 6, are used, one would find the D_{app} for reduction is, in fact, larger than

D_{app} for oxidation of polypyrrole (17). These D_{app} 's are, however, quite misleading because, in the net, the reduction process is slower (Figure 6).

Charge-time transients for base/acid-treated conventional films (Figure 7) are analogous to transients for the untreated films. Again, there is a cross-over in the redox rates, and the rate of the reduction process is ultimately much slower. The charge-time transients for the fibrillar films (Figure 8) are dramatically different; the reduction process is now as fast, if not faster, than the oxidation process throughout the entire duration of the transient (Figure 8).

As noted above, we used the time required to reach 95 percent of the plateau charge (t_{95}) as a measure of the rate of the redox process. Comparisons of t_{95} values between films will only be valid if the films contain the same total quantity of polypyrrole. The quantity of polypyrrole can be controlled by varying the charge delivered during the polymerization process. We prepared various fibrillar and conventional films, containing the same quantity of polypyrrole, so that t_{95} values could be compared.

Reductive t_{95} values are presented in Table I. The fibrillar films show lower t_{95} 's (for each quantity of polypyrrole) than the conventional films. These data clearly indicate that the rate of reductive charge-transport is faster in the fibrillar films than in the conventional films.

The fibrillar films show lower t_{95} 's, in spite of the fact that a comparison of t_{95} 's for the treated vs. untreated conventional films (Table I) indicates that the base/acid treatment slows the rate of charge-transport. That the (treated) fibrillar films show higher reduction rates than the untreated conventional films indicates that the deleterious effect of base/acid treatment is more than compensated by the enhancement due to

optimization of the supermolecular structure.

Oxidative t_{95} values are presented in Tables II. The oxidative t_{95} 's for the fibrillar and conventional films are, within experimental error, identical. This agreement is undoubtedly fortuitous in that a comparison of the treated and untreated conventional films, again, shows that base/acid treatment slows the rate of electron transport. In the oxidative case, the deleterious effect of base/acid treatment is apparently exactly compensated for by the enhancement in charge-transport due to the optimization of the supermolecular structure.

It is also interesting to compare data between Tables I and II. As indicated by the transients in Figures 6 through 8, the reduction rates for the conventional films (either treated or untreated) are always slower than the oxidation rates for these films. In contrast, the reduction and oxidation rates for the fibrillar films are, within experimental error, identical.

Finally, Table III and Table IV present total charge values (Q_{max} 's) associated with oxidation and reduction of all of the films studied here. Each value is the average obtained from a minimum of three polypyrrole films (18). Note that Table III and Table IV show that for any given quantity of polypyrrole, the total charge available for all three types of films are the same. This indicates that neither the base/acid treatment, nor the organization of the polypyrrole chains into narrow fibers changes the stoichiometry of the doping reaction for polypyrrole.

CONCLUSIONS

We have shown that polypyrrole films with a fibrillar supermolecular structure support higher rates of reductive charge-transport than equivalent films with the conventional morphology. It is fortunate that the rate of the

reduction process is enhanced because this corresponds to the discharge reaction in a polypyrrole battery. The data obtained here suggest that batteries incorporating fibrillar polypyrrole cathodes could deliver higher current densities than analogous batteries incorporating conventional polypyrrole cathodes. We are currently exploring this possibility.

In closing, it is also worth noting that higher charge-transport rates are not the only virtue of fibrillar conductive polymers. We have recently shown that extremely narrow conductive polymer fibers show electronic conductivities which are over an order of magnitude higher than the conductivities of the corresponding conventional polymer films (19).

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18. For each individual film, $Q_{\max,ox}$ was slightly greater than $Q_{\max,red}$; this was true even when the oxidation step immediately followed the reduction step. This observed difference is an instrumental artifact which can be explained as follows: The high capacitance of oxidized polypyrrole results in large charging currents at the beginning of the reduction step which overload the measurement system. During this time a small portion of the charge is lost. This problem could, in principle, be solved by decreasing the current sensitivity; however, when this is done, resolution at long time (low currents) is lost. Since we would rather have good resolution at long times, we sacrificed a brief bit of the data at very short times.

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Table I. t_{95} values associated with the reduction of various polypyrrole films.

Quantity of Polypyrrole ^a (μ moles of pyrrole)	t_{95} (sec) ^b		
	Untreated Conventional	Treated ^c Conventional	Fibrillar ^c
0.44	4.0 \pm 1.2	6.6 \pm 1.2	1.7 \pm 0.4
0.88	6.5 \pm 0.4	10.7 \pm 0.7	2.7 \pm 1.6
1.31	7.2 \pm 0.8	12.2 \pm 2.3	3.7 \pm 0.5
1.75	9.3 \pm 0.8	15.3 \pm 0.6	5.9 \pm 2.1

^a Calculated from the charge used for polymerization assuming 2.25 electrons are required for the oxidation of each pyrrole unit incorporated into the film.

^b Time required to reduce the film to 95 % of maximum charge value.

^c Polymer was exposed to base, exposed to acid, rinsed and reduced, see text.

Table II. t_{95} values associated with the oxidation of various polypyrrole films.

Quantity of Polypyrrole ^a (μ moles of pyrrole)	t_{95} (sec) ^b		
	Untreated Conventional	Treated ^c Conventional	Fibrillar ^c
0.44	2.2 \pm 0.4	5.8 \pm 0.7	2.0 \pm 0.5
0.88	4.0 \pm 0.3	6.3 \pm 1.3	2.6 \pm 0.3
1.31	5.3 \pm 0.3	6.8 \pm 1.8	4.7 \pm 0.7
1.75	6.4 \pm 0.6	9.7 \pm 1.9	5.5 \pm 0.5

^a Calculated from the charge used for polymerization assuming 2.25 electrons are required for the oxidation of each pyrrole unit incorporated into the film.

^b Time required to oxidize the film to 95 % of maximum charge value.

^c Polymer was exposed to base, exposed to acid, rinsed and reduced, see text.

Table III. Q_{\max} values associated with the oxidation of various polypyrrole films.

Quantity of Polypyrrole ^a (μ moles pyrrole)	Q_{\max}		
	Untreated Conventional	Treated ^b Conventional	Fibrillar ^b
0.44	10.5 \pm 0.3	11.4 \pm 1.3	10.4 \pm 0.3
0.88	20.7 \pm 0.3	20.5 \pm 1.5	19.0 \pm 2.0
1.31	30.7 \pm 1.0	29.4 \pm 0.3	30.2 \pm 1.8
1.75	37.4 \pm 1.0	38.1 \pm 1.3	41.1 \pm 1.2

^a Calculated from the charge used for polymerization assuming 2.25 electrons per pyrrole unit.

^b Polymer was exposed to base, exposed to acid, rinsed and reduced, see text.

Table IV. Q_{\max} values associated with the reduction of various polypyrrole films.

Quantity of Polypyrrole ^a (μ moles of pyrrole)	Q_{\max}		
	Untreated Conventional	Treated ^b Conventional	Fibrillar ^b
0.44	9.2 \pm 0.9	10.8 \pm 1.2	9.9 \pm 0.3
0.88	18.6 \pm 0.9	18.9 \pm 1.3	19.0 \pm 1.3
1.31	28.0 \pm 1.6	25.7 \pm 0.9	29.1 \pm 1.6
1.75	36.9 \pm 2.1	31.8 \pm 4.3	38.2 \pm 1.5

^a Calculated from the charge used for polymerization assuming 2.25 electrons per pyrrole unit.

^b Polymer was exposed to base, exposed to acid, rinsed and reduced, see text.

Figure Captions

Figure 1 Scanning electron micrograph of surface of Anopore membrane with 0.2 μm pores.

Figure 2 Schematic of preparation of fibrillar polypyrrole. See text for details.

Figure 3 Scanning electron micrograph of fibrillar polypyrrole.

Figure 4 Cyclic voltammograms of 0.5 μm thick conventional polypyrrole film in 0.2 M Et_4BF_4 in acetonitrile at 10 mV sec $^{-1}$.

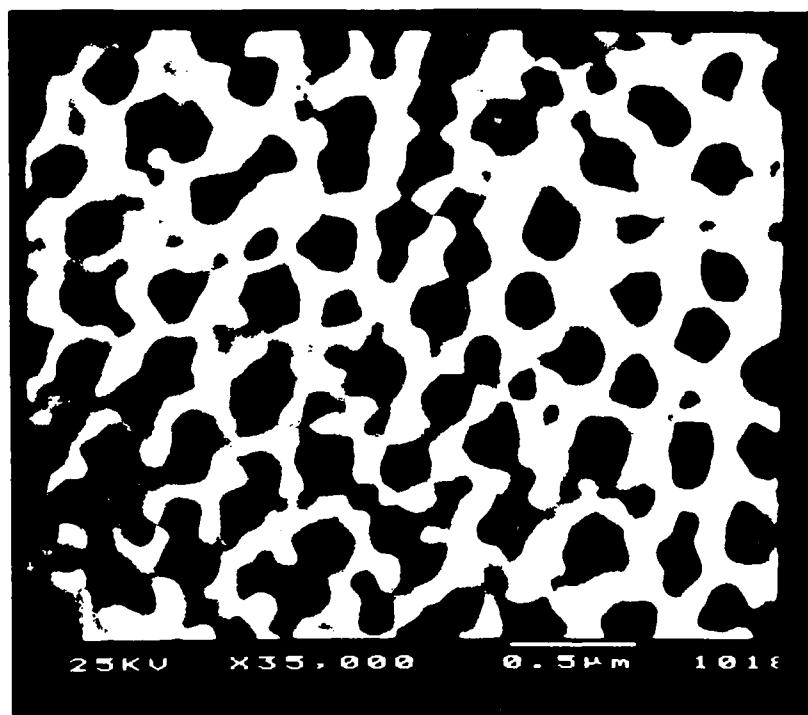
(A) As synthesized film (initial potential -0.8 V). (B) After immersion in 0.2 M NaOH (initial potential -0.8 V, see text). (C) Immediately after immersion in 0.2 M NaOH () and after repeated cycling () (initial potential -1.4 V, see text). (D) After immersion in 1 % HBF₄ (initial potential -0.8 V, see text).

Figure 5 (A) () Cyclic voltammogram of 1.0 μm thick conventional polypyrrole film after immersion in 0.2 M NaOH and 1% HBF₄ (initial potential -0.8 V, scan rate 10 mV sec $^{-1}$). (B) () Equivalent amount of fibrillar polypyrrole treated in the same way (initial potential -0.8 V, scan rate 10 mV sec $^{-1}$).

Figure 6 Charge vs. time transients for a conventional 1.0 μm thick polypyrrole film (0.88 μmole pyrrole).

Figure 7 Charge vs. time transients for a conventional 1.0 μm thick polypyrrole film (0.88 μmole pyrrole) treated with base and acid (see text).

Figure 8 Charge vs. time transients for fibrillar polypyrrole (0.88 μmole pyrrole) (see text).



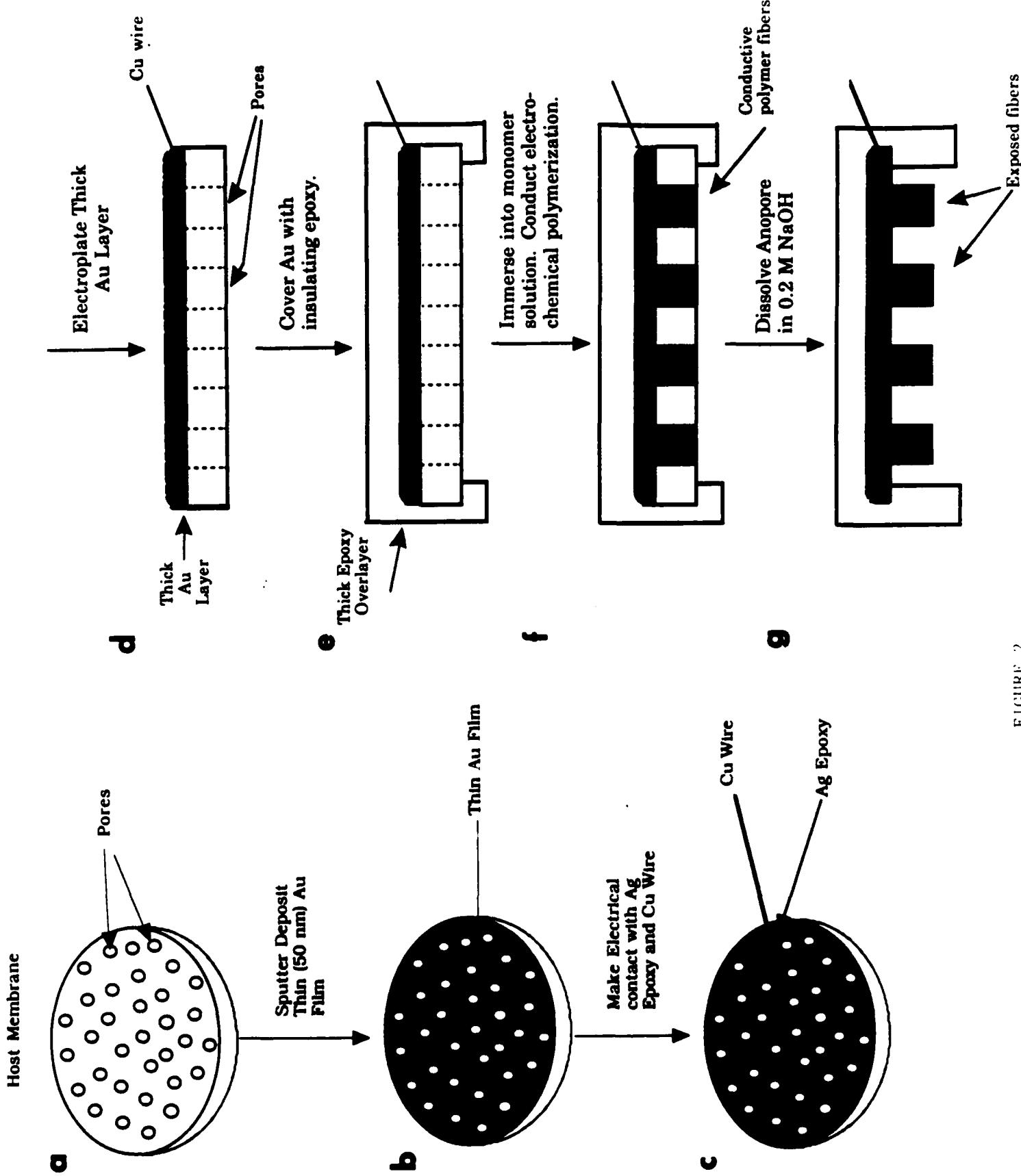
25KV

X35,000

0.5 μ m

1018

Fig 2



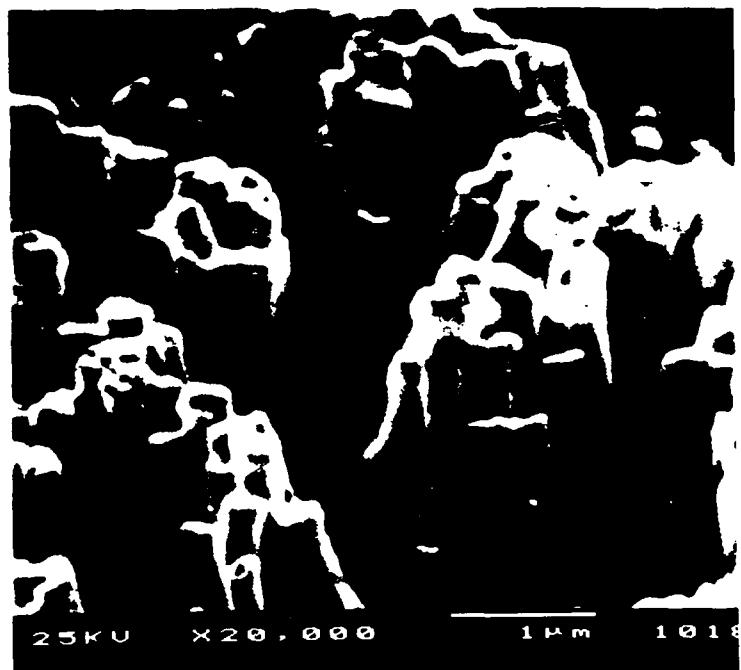
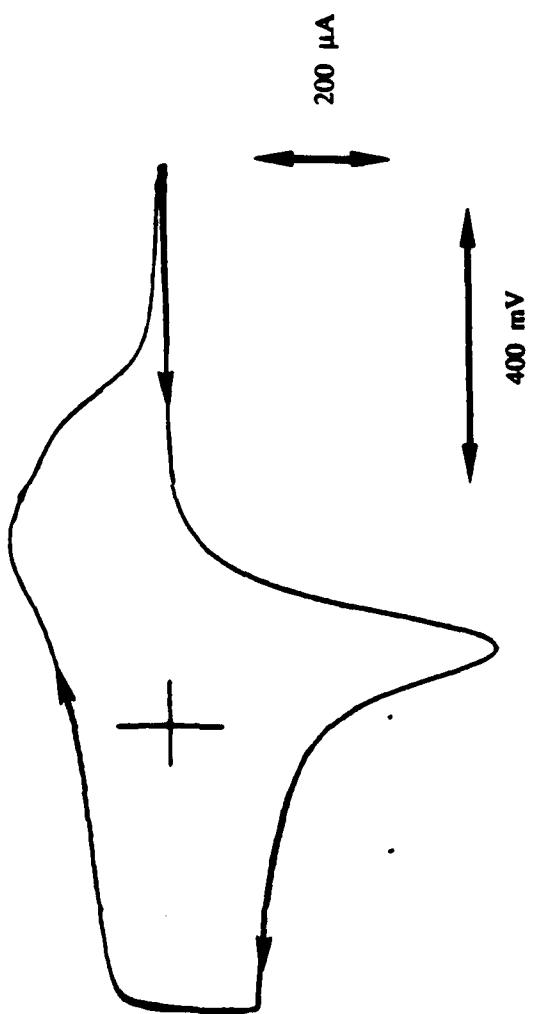
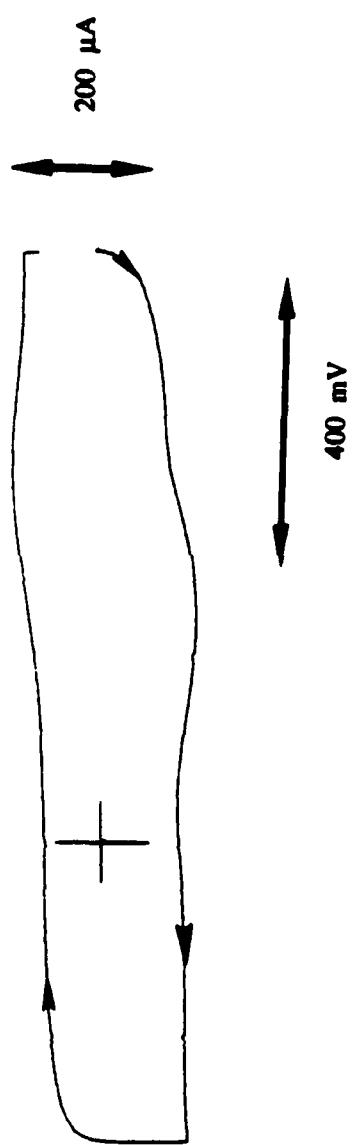


Fig 3





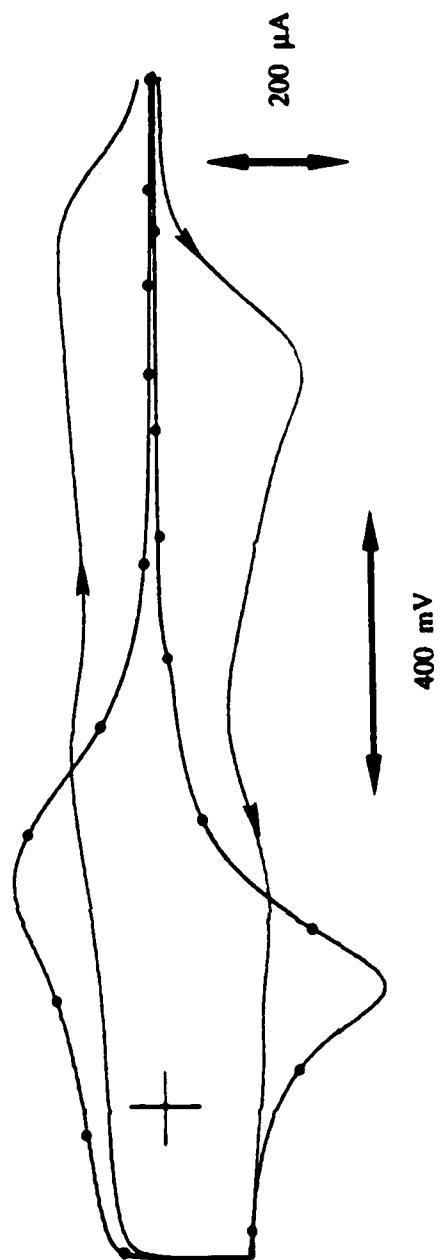


Fig. 4.5

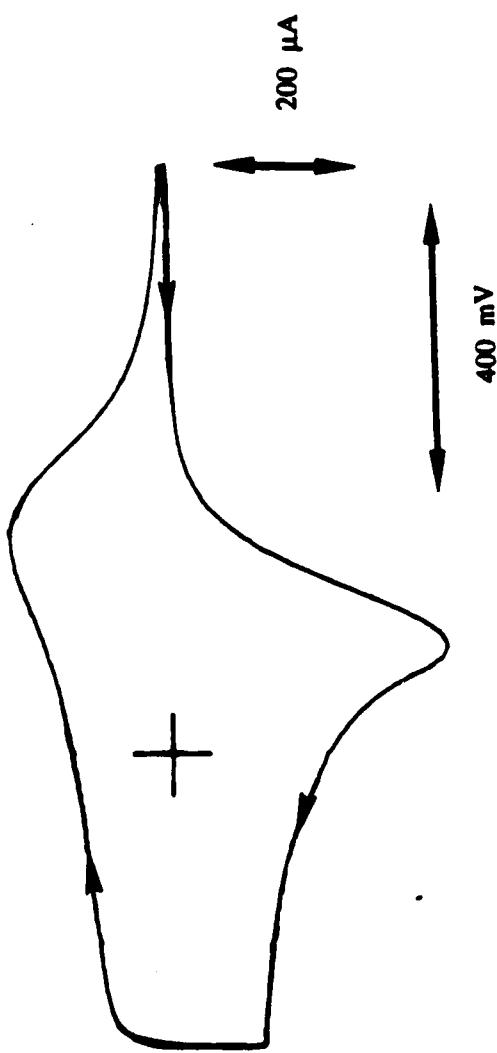
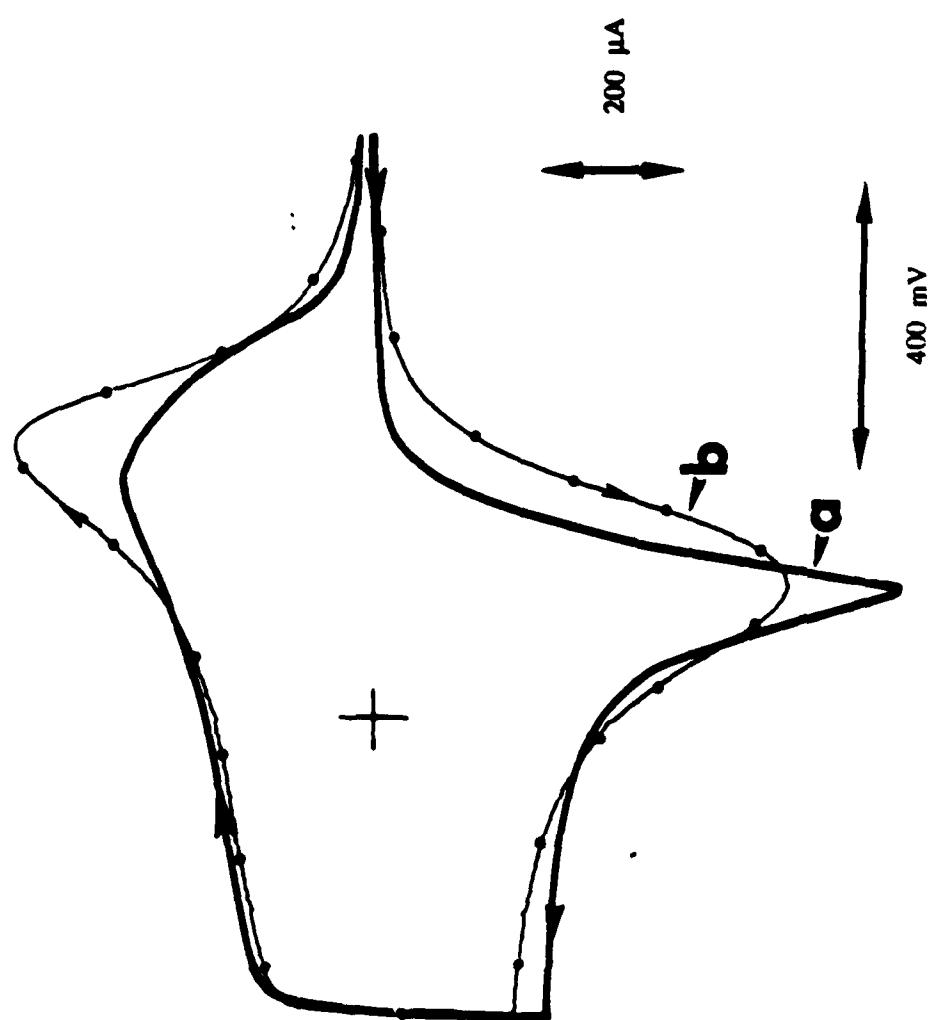


Fig 4D



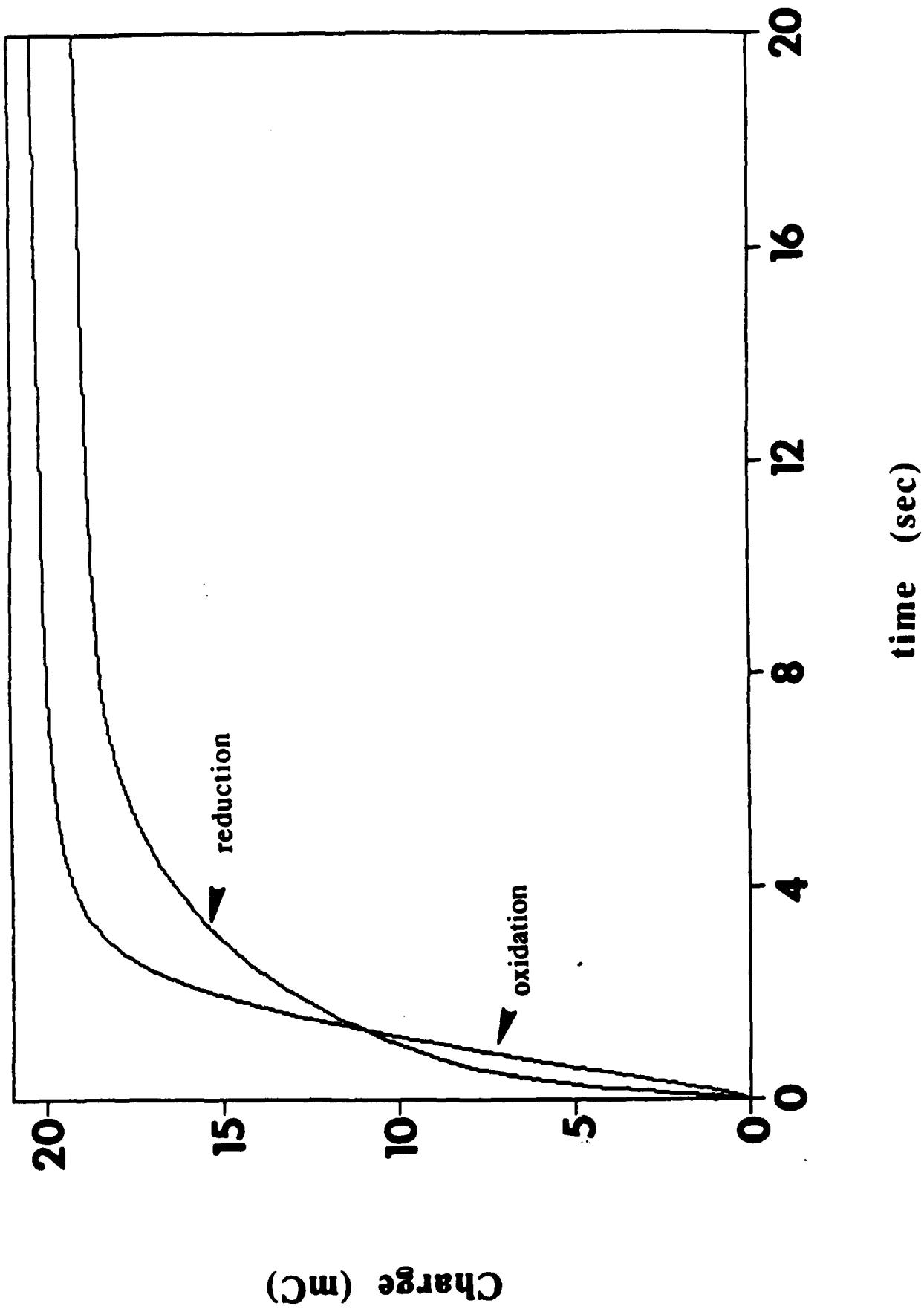


Fig. 6

